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~~Film and its use to coat moldings~~

The present invention relates to a film having at least one support layer and at least one coating layer.

The use of films to coat exterior automobile parts is of increasing interest owing in particular to progress in thermoforming and in the technology of the "in-mold decoration" of polymer moldings (E. Bürkle in Kunststoffe 87 (1997), 320-328; Modern Plastics International 11 (1997), 33-34; G. Steinbichler and J. Gießauf in Kunststoffe 87 (1997), 1262-1270).

State of the art are multilayer films whose transparent layer comprises thermoplastic polymers, e.g., polyvinylidene fluoride (PVdF). Such films are available commercially, for example, as "in-mold surfacing film" from 3M/REXAM. WO 94/09983 and EP 361823 (AVERY DENNISON Corp.) describe multilayer films whose transparent layers comprise PVdF/polyacrylate blends and whose pigmented color layers based on PVdF or polyvinyl chloride are applied thereto directly or via a tie layer. Via an adhesive layer, these assemblies are applied to the molding to be provided with the film, after an optional support layer has been removed beforehand. Disadvantages of these films are the high halogen content of about 60% by weight (ecology and price) and also the inadequate service properties of the very soft transparent layers.

Furthermore, lacking sufficient extrudability, the PVdF-based layers are preferably applied from organic solution, necessitating a predetermined coating sequence of 1. transparent layer, 2. base layer, in order to prevent bleeding phenomena in the bottom, effect layer, which is applied first, which would otherwise cause changes in shade and effect. Also known are transparent layers of thermoplastic polymethyl methacrylate (PMMA), obtained preferably by coextrusion with the support layer and/or base layer (A. Grefenstein in Kunststoffe 87 (1997), 1332-1343). However, because of the high glass transition temperature, these layers tend toward brittleness and/or require narrow processing windows for the deformation and handling of the films. Moreover, certain service properties of such layers do not meet the requirements imposed on high-grade transparent layers.

EP 251 546 describes a process for coating automobile parts with a coated film. The film comprises a colored coating material which has been cured thermally beforehand. In EP 361 351 this process is implemented with radiation-curable coating materials, in order not to deform the thermoplastic support films as a result of high temperatures.

The technical problem is to combine the film properties in the initial state (on the roll - nonflowing, nontacky, free from blocking) with the necessary thermoformability of the film during

processing (extensions of more than 100%) and the desired service properties of the article provided with the film (especially the mechanical strength and chemical resistance). To solve this problem, the patent literature describes approaches which produce and process films possessing latent curability in usually one layer, and in which the film, following its application, is cured to completion.

WO 96/10059 describes two-layer films which possess latent heat curability and are flowable in the melt, these films being used to seal metallic joints in automobile construction. On heating, the bottom layer expands and the top layer flows and, after curing, encloses the bottom layer.

The document DE 196 33 959 describes a process of radiation-induced curing of a protective layer which beforehand, as the outer layer of a preformed, multilayer decorative film, has been backsprayed in the injection mold with a thermoplastic. The resin composition of the protective layer in the uncured state comprises an acrylic copolymer main chain having a glass transition temperature of from 40 to 120°C and an average molecular weight (Mw) of preferably from 45 000 to 80 000 and also at least one (meth)acryloyl-functional side chain which is provided with an at least trifunctional crosslinker, containing (meth)-acryloyl groups, and a photoinitiator.

As a result of the high glass transition point and the comparatively low functionality of (meth)acryloyl

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groups of the polymer in the protective layer, the service properties of the films obtained following inventive irradiation of the applied decorative film are inadequate for the stringent requirements imposed on exterior automobile parts. Moreover, because of the high molecular weights of the main polymer, application can be made only from organic solution. Furthermore, the high expectations which exist in automobile construction cannot be met with the single-layer solutions proposed in the document.

The documents DE 196 54 918 A1 and DE 196 28 966 C1 (DAIMLER BENZ) propose partially curing a coating film on the film composite, which is then to be processed (i.e., rolled up) with a glass transition temperature of less than 40°C, in particular less than 30°C, without adhesion and can be thermoformed at temperatures slightly above the glass transition point. The finished part with the aforementioned layer, which has thus then been provided with a film, is subsequently subjected to final curing with electromagnetic radiation in order to ensure the service properties. Materials proposed and claimed for the exterior layer (i.e., transparent layer) applied and processed in this way include phosphazines, polyacrylates and polyurethanes as polymeric "binders". A disadvantage which may be mentioned for the solution described is that the uncured or part-cured film is intended to represent a continuous layer whose glass transition temperature is intended to lie within a

certain, very low temperature range in order to ensure simultaneously blocking resistance (absence of adhesion) and thermoformability (formability). Accordingly, the solution represents a classic
5 compromise between contradictory physical requirements (absence of adhesion, and stretchability). The degrees of freedom in the selection of suitable materials are therefore very low.

For the lamination of exterior automobile parts
10 there is therefore a need for multilayer films which as far as possible can be produced without solvent and without using halogenated thermoplastic polymers, which can be stored as blocking-resistant, nonflowing, windable stock, which during processing can be
15 thermoformed to give formings and which during or after application to the workpiece - either by vacuum-assisted lamination or by backspraying with thermoplastics in a mold - can be crosslinked to give smoothly leveled films, and whose appearance (shade and
20 effect range of the known automotive OEM coating materials) and service properties meet the present requirements of the automobile industry as regards OEM coating systems.

It is an object of the present invention,
25 therefore, to provide a film composite comprising a support layer and at least one coating layer applied thereon, which no longer has the problems indicated.

This object is achieved by the presence of at least one coating layer which is based on a powder coating material or on a powder coating dispersion.

In accordance with the invention, the layer
5 based on the powder coating material or the powder coating dispersion may be applied directly to the support layer. Preferably, a layer based on a liquid coating material is applied, on to which the powder coating material or the powder coating dispersion is
10 coated. Additionally, a surface layer and also a removable cover film may be present. Accordingly, the invention may result in a film composite comprising a support film layer, an optional surfacer, an optional liquid coating, a layer based on a powder coating
15 material or a powder coating dispersion, and an optional transparent polymer film.

For example, the following variants may also be considered:

1. Optional adhesive layer, support film layer,
20 optional surfacer (primer), pigmented liquid coating layer, powder clearcoat layer, optional removable film.
2. Removable film, powder clearcoat layer, pigmented liquid coating layer, optional surfacer (primer)
25 and/or adhesive, optional removable film.

Suitable materials for the layer based on a powder coating material are in principle all organic polymers known from paint chemistry. The selection is guided by the requirements specific to the application.

examples being the weather resistance and UV stability, intrinsic color, etc. Material to the invention are the requirements relating to the melting characteristics of the particles and to the ability for chemical,
5 substantially emission-free crosslinking in the melt. Preferably, powder coating materials and aqueous suspensions of polymer powders are produced and processed in accordance with known processes.

A powder coating material which can be used in
10 accordance with the invention may comprise, for example:

- a) at least one epoxide-containing binder containing from 20 to 45% of glycidyl-containing monomers accompanied, if desired, by vinylaromatic
15 compounds, preferably styrene,
- b) crosslinking agents,
- c) if desired, catalysts, auxiliaries, additives typical of powder clearcoat materials, such as devolatiliziers, leveling agents, UV absorbers,
20 free-radical scavengers, antioxidants.

Preference is given in this context to the following proportions:

- a) 60-80 parts
- b) 15-30 parts
- 25 c) 3-10 parts

Examples of a suitable epoxy-functional binder for the solid powder clearcoat material are polyacrylate resins containing epoxide groups, which are preparable by copolymerizing at least one

ethylenically unsaturated monomer containing at least one epoxide group in the molecule with at least one further ethylenically unsaturated monomer containing no epoxide group in the molecule, at least one of the monomers being an ester of acrylic acid or methacrylic acid. Polyacrylate resins of this kind containing epoxide groups are known, for example, from EP-A-299 420, DE-B-22 14 650, DE-B-27 49 576, US-A-4,091,048 and US-A-3,781,379.

Examples of ethylenically unsaturated monomers which contain no epoxide group in the molecule are alkyl esters of acrylic and methacrylic acid which contain 1 to 20 carbon atoms in the alkyl radical, especially methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, butyl acrylate, butyl methacrylate, 2-ethylhexyl acrylate and 2-ethylhexyl methacrylate. Further examples of ethylenically unsaturated monomers which contain no epoxide groups in the molecule are acid amides, such as acrylamide and methacrylamide, for example, vinylaromatic compounds, such as styrene, methylstyrene and vinyltoluene, nitriles, such as acrylonitrile and methacrylonitrile, vinyl halides and vinylidene halides, such as vinyl chloride and vinylidene fluoride, vinyl esters, such as vinyl acetate, for example, and hydroxyl-containing monomers, such as hydroxyethyl acrylate and hydroxyethyl methacrylate, for example.

The epoxide-functional monomers used in the epoxide-functional binders are preferably glycidyl,

acrylate, glycidyl methacrylate and allyl glycidyl ether.

The polyacrylate resin containing epoxide groups normally has an epoxide equivalent weight of
5 from 300 to 2 500, preferably from 420 to 700, a number-average molecular weight (determined by gel permeation chromatography using a polystyrene standard) of from 2 000 to 20 000, preferably from 3 000 to 10 000, and a glass transition temperature (T_g) of from
10 30 to 80, preferably from 40 to 70, with particular preference from 40 to 60°C (measured with the aid of Differential Scanning Calorimetry (DSC)). Very particular preference is given to approximately 50°C. It is also possible to employ two or more acrylate
15 resins.

The polyacrylate resin containing epoxide groups may be prepared by widely known methods, by addition polymerization.

Preference is given in accordance with the
20 invention to the methyl/butyl mixed esters. These have the advantage over straight methyl esters of better solubility in polymer melts, and also to butyl/ethylhexyl mixed esters. Preference is also given, in accordance with the invention, to the
25 straight butyl esters.

As crosslinkers, various blocked polyisocyanates may be suitable. It is also possible to employ amino resins, e.g., melamines.

In principle, any amino resin suitable for transparent topcoat materials, or a mixture of such amino resins, may be used.

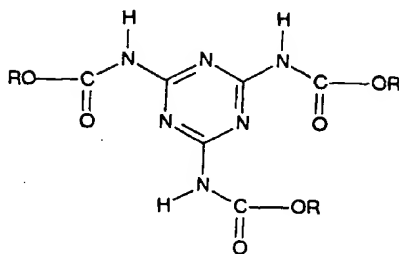
Resins of this kind are well known to the skilled worker and are offered by numerous companies as commercial products. Amino resins are condensation products of aldehydes, especially formaldehyde, and urea, melamine, guanamine and benzoguanamine, for example. The amino resins contain alcohol groups, preferably methylol groups, which in general are fully or partly etherified with alcohols.

Suitable further crosslinkers are carboxylic acids, especially saturated, straight-chain, aliphatic dicarboxylic acids having 3 to 20 carbon atoms in the molecule. Very particular preference is given to the use of dodecane-1,12-dioic acid. To modify the properties of the finished powder clearcoat materials it is possible, if desired, to use other carboxyl-containing crosslinkers. Examples that may be mentioned include saturated branched or unsaturated straight-chain dicarboxylic and polycarboxylic acids, and also polymers containing carboxyl groups.

Also suitable are powder clearcoat materials which comprise an epoxy-functional crosslinker and an acid-functional binder.

As component (b) it is also possible to use tris(alkoxycarbonylamino)triazines in accordance with US-A 4,939,213, US-A 5,084,541 and EP 0 624 577.

These are tris(alkoxycarbonylamino)triazines of the formula



where R = methyl, butyl, ethylhexyl groups. Derivatives
5 of these compounds may also be used.

The abovementioned crosslinking agents may also
be used as a mixture of one or more of the
abovementioned compounds. When making the selection it
should, however, be ensured that no significant
10 condensation products are formed during the subsequent
thermal steps unless they are able to escape (e.g., in
the injection mold or below a protective film).

Examples of suitable acid-functional binders
are acidic polyacrylate resins which can be prepared by
15 copolymerizing at least one ethylenically unsaturated
monomer containing at least one acid group in the
molecule with at least one further ethylenically
unsaturated monomer containing no acid group in the
molecule.

20 The binder containing epoxide groups and the
crosslinker containing carboxyl groups, or,
respectively, the carboxyl binder and epoxy
crosslinker, are normally used in an amount such that
there are from 0.5 to 1.5, preferably from 0.75 to

1.25, equivalents of carboxyl groups per equivalent of epoxide groups. The amount of carboxyl groups present can be determined by titration with an alcoholic KOH solution.

5 In accordance with the invention, the binder comprises vinylaromatic compounds, especially styrene. In order to limit the risk of cracking on weathering, however, the amount is not more than 35% by weight. From 10 to 25% by weight is preferred.

10 If desired, the solid powder coating materials comprise one or more suitable catalysts for the epoxy resin curing. Suitable catalysts are phosphonium salts of organic or inorganic acids, quaternary ammonium compounds, amines, imidazole and imidazole derivatives.

15 The catalysts are generally used in proportions of from 0.001% by weight to about 2% by weight, based on the overall weight of the epoxy resin and the crosslinking agent.

 Examples of suitable phosphonium catalysts are
20 ethyltriphenylphosphonium iodide, ethyltriphenylphosphonium chloride, ethyltriphenylphosphonium thiocyanate, ethyltriphenylphosphonium acetate-acetic acid complex, tetrabutylphosphonium iodide, tetrabutylphosphonium bromide and tetrabutylphosphonium acetate-
25 acetic acid complex. These and other suitable phosphonium catalysts are described, for example, in US-A 3,477,990 and US-A 3,341,580.

 Examples of suitable imidazole catalysts are 2-styrylimidazole, 1-benzyl-2-methylimidazole, 2-methyl-

imidazole and 2-butylimidazole. These and other imidazole catalysts are described, for example, in the Belgian patent no. 756,693.

Furthermore, the solid powder coating materials
5 may also, if desired, comprise auxiliaries and additives. Examples thereof are leveling agents, antioxidants, UV absorbers, free-radical scavengers, free-flow aids and devolatilizers, such as benzoin, for example.

10 The solid powder coating materials are prepared in accordance with known methods (cf., e.g., product information bulletin from BASF Lacke + Farben AG, "Pulverlacke" [Powder coating materials], 1990) by homogenization and dispersion using, for example, an
15 extruder, screw kneading device and the like. Following preparation of the powder coating materials, they are prepared for dispersion by milling and, if appropriate, by classifying and sieving.

The powder clearcoat material may also be
20 present in the form of an aqueous dispersion. This dispersion preferably comprises a component A in the form of the solid powder coating material and an aqueous component B. Particular preference is given to an aqueous powder clear coat dispersion comprising
25 a solid, pulverulent component A and an aqueous component B, where component A is a powder clearcoat material comprising
a) at least one epoxide-containing binder containing from 20 to 45%, preferably from 25 to 35% of

glycidyl-containing monomers, accompanied if desired by vinylaromatic compounds, preferably styrene,

- b) crosslinking agents, and
- 5 c) if desired, catalysts, auxiliaries, additives typical of powder clearcoat materials, such as devolatiliziers, leveling agents, UV absorbers, free-radical scavengers, antioxidants and

10 component B is an aqueous dispersion comprising

- a) at least one, preferably nonionic, thickener, and
- b) if desired, catalysts, auxiliaries, defoamers, dispersing auxiliaries, wetting agents, preferably carboxy-functional dispersants, antioxidants, UV
- 15 absorbers, free-radical scavengers, small amounts of solvent, leveling agents, biocides and/or water retention agents.

In accordance with the invention, preference is given to the following proportions for the components A
20 and B:

Component A

- a) 60-80 parts
- b) 15-30 parts
- 25 c) 3-10 parts

Component B

- a) 20-50 parts of component A
- b) 80-50 parts of component B

c) 1 000-5 000 parts of distilled water

The dispersion contains preferably 25-100 parts of component A and 100 parts of component B.

5 Preference is given in accordance with the invention to nonionic associative thickeners a).

Structural features of such associative thickeners a) are:

aa) a hydrophilic framework, which ensures sufficient
10 solubility in water, and

ab) hydrophobic groups, which are capable of associative interaction in the aqueous medium.

Examples of hydrophobic groups used are long-chain alkyl radicals, such as dodecyl, hexadecyl or
15 octadecyl radicals, for example, or alkaryl radicals, such as octylphenyl or nonylphenyl radicals, for example.

Hydrophilic frameworks used are preferably polyacrylates, cellulose ethers or, with particular
20 preference, polyurethanes, containing the hydrophobic groups as polymer building blocks.

Very particularly preferred hydrophilic frameworks are polyurethanes containing polyether chains as building blocks, preferably comprising polyethylene oxide.

25 In the synthesis of such polyether polyurethanes, the diisocyanates and/or polyisocyanates, preferably aliphatic diisocyanates, with particular preference unsubstituted or alkyl-substituted 1,6-hexamethylene diisocyanate, are used to link the hydroxyl-terminated

polyether building blocks with one another and to link the polyether building blocks with the hydrophobic end-group building blocks, which may, for example, be monofunctional alcohols and/or amines containing the
5 abovementioned long-chain alkyl radicals or aralkyl radicals.

The dispersing auxiliaries which may be used with preference in component B include polyurethanes.

These may preferably comprise

- 10 1. at least one organic component containing at least two reactive hydrogen atoms,
2. a monofunctional ether, and
3. a polyisocyanate.

The organic component of the polyurethane
15 composition comprises a polyester polyol, a low molecular mass diol and/or triol, or mixtures thereof. If desired, a trifunctional monomer containing hydroxyl groups may be used.

In a second preferred embodiment, the
20 polyurethane comprises

1. at least one organic component containing at least two reactive hydrogen atoms,
2. a nonionic stabilizer prepared by reacting
 - 25 i. a monofunctional polyether with a polyisocyanate component, in order to produce an isocyanate intermediate, and
 - ii. a component containing at least one active amine group and at least two active hydroxyl groups, and

3. at least one polyisocyanate component.

The organic component preferably comprises polyether polyester polyol, a low molecular mass diol and/or triol, or mixtures thereof.

5 The polyester component may be prepared by reacting at least one dicarboxylic acid and at least one alcohol component, the alcohol containing at least two hydroxyl groups. The carboxylic acid component contains two or more carboxyl groups.

10 In addition to the carboxylic acid, the polyester resin may also include one or more low molecular mass diols or triols. Any polyol may be used in principle.

The polyester resins or mixtures of polyester
15 resins that are used preferably contain terminal hydroxyl groups. This is brought about by adding an excess of polyols.

To synthesize the polyesters it is possible to use both monocarboxylic acids and monoalcohols.
20 Preferably, however, the monocarboxylic acids and/or monoalcohols are present in the polyester resin in a very low amount by weight.

The polyester diol components preferably used contain between 20 and 80% by weight of the
25 polyurethane resin. The amounts are preferably between 50 and 70% by weight. Very particular preference is given to from 55 to 65% by weight.

To prepare the polyurethane, polyester polyols having a molecular weight of between 500 and 5 000 are

used." Preference is given to molecular weights of between 1 000 and 3 500.

In addition to the polyester diols, the polyurethane resins may contain further organic components containing at least two reactive hydrogen atoms. These are preferably diols and triols, thiols and/or amines, or mixtures of these substances. The components used to synthesize the polyester component may also be employed as separate components in this case. In other words, dialcohols or trialcohols, such as neopentyl glycol or 1,6-hexanediol, for example, are also suitable as an additional organic component in the polyurethane.

The molecular weight of the diols and/or triols used in the polyurethane resin is between 0 and 20% by weight. From 1 to 6% by weight is preferred.

The polyurethane resin further comprises polyisocyanates, especially diisocyanates. The isocyanates are present at between 5 and 40% by weight, based on the polyurethane mass. Particular preference is given to from 10 to 30% by weight and very particular preference to from 10 to 20% by weight. To prepare the polyurethane, finally, a monofunctional polyether is used.

In a second variant, a nonionic stabilizer is prepared in which, preferably, a monofunctional polyether is reacted with a diisocyanate. The reaction product formed is then reacted with a component

containing at least one active amine group and at least two active hydroxyl groups.

In one particular embodiment, the polyurethane comprises a reaction product of:

- 5 1. a polyester polyol, in turn comprising a reaction product of a carboxylic acid containing at least two carboxyl groups and a component containing at least two hydroxyl groups,
2. at least one low molecular mass component
- 10 containing at least two hydroxyl groups,
3. at least one polyisocyanate component,
4. a nonionic stabilizer prepared by reacting a monofunctional ether with a polyisocyanate and then reacting the resulting reaction product with
- 15 a component containing at least one active amine and at least two active hydroxyl groups.

In a fourth variant, the polyurethane comprises a reaction product of

1. a polyester polyol,
- 20 2. at least one low molecular mass diol or triol,
3. a polyisocyanate,
4. a monomer containing trihydroxy groups,
5. a monofunctional hydroxyl-containing polyether.

The polyesters are synthesized with the above-
25 described carboxylic acid components and an excess of polyols. The excess of polyols is chosen so as to give, preferably, terminal hydroxyl groups. The polyols preferably have a hydroxyl functionality of at least two.

The polyester resin preferably comprises one or more polyols, preferably a diol. Diols used with preference are alkylene glycols, such as ethylene glycol, propylene glycol, butylene glycol and neopentyl glycol, 1,6-hexanediol or other glycols, such as bisphenol A, cyclohexanedimethanol, caprolactonediol, hydroxyalkylated bisphenol and similar compounds.

The low molecular mass diols that are preferably used in accordance with the invention are known from the prior art. They include aliphatic diols, preferably alkylene polyols having 2 to 18 carbon atoms. Examples thereof are 1,4-butanediol, cycloaliphatic diols, such as 1,2-cyclohexanediol and cyclohexanedimethanol.

Organic polyisocyanates suitable in accordance with the invention are preferably those containing at least two isocyanate groups. Particular preference is given to diisocyanates, e.g., p-phenylene diisocyanate, 4,4'-biphenyl diisocyanate, toluene diisocyanate, 3,3'-dimethyl-4,4'-biphenylene diisocyanate, 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, 2,2,4-trimethylhexane 1,6-diisocyanate, methylenebis(phenyl isocyanates), 1,5-naphthalene diisocyanate, bis(isocyanatoethyl fumarate), isophorone diisocyanate and methylenebis(4-cyclohexyl isocyanate).

Besides the abovementioned diisocyanates, other polyfunctional isocyanates are also used. Examples are 1,2,4-benzene triisocyanate and polymethylene-polyphenyl isocyanates.

Particular preference is given to the use of aliphatic diisocyanates, e.g., 1,6-hexamethylene diisocyanate, 1,4-butylene diisocyanate, methylene-bis(4-cyclohexyl isocyanate), isophorone diisocyanate and 2,4-toluene diisocyanate.

Longer-chain polyurethane resins may be obtained by chain extension with components containing diol and/or triol groups. Particular preference is given to chain extenders containing at least two active hydrogen groups, examples being diols, thiols, diamines or mixtures of these substances, e.g., alkanolamines, aminoalkyl mercaptans, hydroxyalkyl mercaptans and similar compounds.

Examples of diols used as chain extenders are 1,6-hexanediol, cyclohexanedimethylol and 1,4-butanediol. A particularly preferred diol is neopentyl glycol.

The polyethers which can be used are preferably monofunctional or difunctional polyethers. Examples of the monofunctional ones include those prepared by polymerizing ethylene oxides, propylene oxides or mixtures thereof.

The polyurethane product described may be mixed with conventional crosslinkers. These include, preferably, amino resins, e.g., melamine. It is also possible to use condensation products of other amines and amides, examples being aldehyde condensates of triazines, diazines, triazoles, guanidines, guanamines or alkyl- and aryl-substituted derivatives of such

components. Some examples of such components are N,N'-dimethylurea, dicyandiamides, 2-chloro-4,6-diamino-1,3,5-triazine, 6-methyl-2,4-diamino-1,3,5-triazine, 3,5-diaminotriazole, triaminopyrimidines, 2-mercapto-
5 4,6-diaminopyrimidine, 2,4,6-triethyltriamino-1,3,5-triazine and similar substances.

Suitable aldehydes are preferably formaldehyde. It is likewise possible to use acetaldehyde, crotonaldehyde, acrolein, benzaldehyde, furfural.

10 The amine-aldehyde condensation products may include methylol or similar alcohol groups. Examples of alcohols that can be used are methanol, ethanol, propanol, butanol, pentanol, hexanol, heptanol, benzyl alcohol and aromatic alcohols, cyclic alcohols, such as
15 cyclohexanol, monoethers or glycols, and also substituted alcohols, e.g., 3-chloropropanol.

In addition to the abovementioned isocyanates it is also possible to use blocked polyisocyanates as crosslinking agents. Examples of these include organic
20 polyisocyanates such as trimethylene, tetramethylene, hexamethylene, 1,2-propylene, 1,2-butylene and 2,3-butylene diisocyanates. Likewise suitable for use are cycloalkene components such as 1,3-cyclopentane, 1,4-cyclohexane and 1,2-cyclohexane diisocyanates. It
25 is also possible to use aromatic components such as phenylene, p-phenylene, 4,4'-biphenyl, 1,5-naphthalene and 1,4-naphthalene diisocyanates. Also suitable, furthermore, are aliphatic-aromatic components such as 4,4'-diphenylenemethane, 2,4- or 2,6-tolylene or

- mixtures thereof, 4,4'-toluidine and 1,4-xylylene diisocyanates. Further examples are ring-substituted aromatic components such as 4,4'-diphenyl ether diisocyanates and chlorodiphenylene diisocyanates.
- 5 Triisocyanates which can be used are triphenylmethane 4,4'4''-triisocyanate, 1,3,5-triisocyanatobenzene and 2,4,6-triisocyanatotoluene. Tetraisocyanates which may be used, finally, include 4,4'-diphenyldimethylmethane 2,2',5,5'-tetraisocyanate.
- 10 Blocking agents which can be used include aliphatic, cycloaliphatic and aromatic alkyl monoalcohols. Examples include methyl, ethyl, chloroethyl, propyl, butyl, cyclohexyl, heptyl, octyl and nonyl alcohols, 3,3,5-trimethylhexanol, decyl
- 15 alcohol and lauryl alcohol. Examples of phenolic components which can be used are phenols or substituted phenols. Examples thereof are cresol, xlenol, nitrophenol, chlorophenol, ethylphenol, 1-butylphenol and 2,5-di-t-butyl-4-hydroxytoluene.
- 20 Further suitable blocking agents are tertiary hydroxylamines, e.g., diethylethanolamine and oximes, such as methyl ethyl ketone oxime, acetone oxime and cyclohexanone oxime.

The crosslinking agents described are present

25 in the polyurethane dispersion in amounts from 2 to 15% by weight, preferably from 4 to 8% by weight.

The polyurethane obtained may be present in the powder slurry with a proportion of from 2 to 20% by weight, preferably from 5 to 15% by weight.

The aqueous powder clearcoat dispersion may be prepared from the components A and B by wet milling or by stirred incorporation of dry-milled powder coating material. Particular preference is given to wet
5 milling.

Following the dispersion of component A in component B, milling is carried out if appropriate, the pH is adjusted to 4.0-7.0, preferably 5.5-6.5, and the dispersion is filtered.

10 The average particle size is between 1 and 25 μm , preferably less than 20 μm , with particular preference from 3 to 10 μm . The solids content of the aqueous powder clearcoat dispersion is between 15 and 50%.

15 Before or after the wet milling and/or the introduction of the dry powder coating material into the water, from 0 to 5% by weight of a defoamer mixture, an ammonium and/or alkali metal salt, a dispersing auxiliary, wetting agent and/or thickener
20 mixture, and also the other additives, may be added to the dispersion. In accordance with the invention, defoamers, dispersing auxiliaries, wetting agents and/or thickeners are preferably first dispersed in water. Then small portions of the powder clearcoat
25 material are stirred in. Subsequently, defoamers, dispersing auxiliaries, thickeners and wetting agents are again incorporated by dispersion. Finally, small portions of powder clearcoat materials are again stirred in.

In accordance with the invention, the adjustment of the pH is carried out preferably using ammonia or amines. In this case, the pH may initially rise, so that a strongly basic dispersion is formed. However, over the course of several hours or days, the pH drops back to the values indicated above.

Another variant for preparing the powder clearcoat dispersion of the invention comprises mixing a liquid melt of the binders and crosslinkers and, if desired, of the additives c) with component A, in an emulsifying apparatus, preferably with the addition of water and stabilizers, cooling the resulting emulsion and filtering it.

As material for the layer based on the liquid coating material, which may be present, if desired, between film and powder coating layer, all coating systems currently in existence are suitable.

In particular, it is possible to use any basecoat material suitable for the conventional coating of automobile bodies. A prerequisite, however, is good flexibility of the cured coating material, without any loss of resistance to stone chipping and corrosion. Coating materials of this kind are well known to the skilled worker. They essentially comprise a polymeric binder, an optional crosslinking agent, and also a pigment or a mixture of pigments.

As its binder, the basecoat material which can be employed in accordance with the invention may comprise, for example, a polyester resin, a

polyurethane resin or a polyacrylate resin, or a mixture of such binders.

In particular, the liquid coating material may further comprise rheological agents and also other coating auxiliaries. It is of course also possible for pigments of any kind, examples being color pigments such as azo pigments, phthalocyanine pigments, carbonyl pigments, dioxazine pigments, titanium dioxide, pigmentary carbon black, iron oxides and chromium and/or cobalt oxides, or effect pigments such as metal flake pigments, especially aluminum flake pigments, and pearlescent pigments, to be incorporated, and/or liquid-crystalline polymers.

Furthermore, the liquid coating materials which can be employed may, if desired, comprise further customary auxiliaries, additives, suitable light stabilizers (e.g., HALS compounds, benzotriazoles, oxalanilide and the like), slip additives, polymerization inhibitors, flattening agents, defoamers, leveling agents and film-forming auxiliaries, e.g., cellulose derivatives, or other additives commonly employed in basecoat materials. These customary auxiliaries and/or additives are usually used in an amount of up to 15% by weight, preferably from 2 to 9% by weight, based on the weight of the coating material without pigments and without fillers.

Finally, the liquid coating material may also contain adhesion promoting agents, in order to improve the bond between films and powder coating material.

Particularly suitable for this purpose are functional silanes, (transition) metal complexes and their alkoxides, polyamines, halogenated and/or polar-modified polyolefins (e.g., in accordance with
5 EP 0 755 422), and amphiphilic block copolymers.

Here again, however, a prerequisite is good flexibility of the cured coating material without any loss of the resistance to stone chipping and corrosion. Coating materials of this kind are well known to the
10 skilled worker.

As crosslinking agent, the basecoat material may comprise an amino resin, a polyisocyanate resin, a carboxyl-containing crosslinking agent, or a mixture of such crosslinking agents.

15 Also suitable are tris(alkoxycarbonylamino)triazines. It is likewise possible to use derivatives thereof. With preference it is possible to use tris(alkoxycarbonylamino)triazines as are described in US-A 5084541.

20 The dry film thickness of the applied liquid coating film should be between 15 and 200 μm , preferably between 50 and 100 μm .

The dry film thickness of the applied film based on powder coating material or on powder coating
25 dispersions should be between 30 and 200 μm , preferably between 50 and 100 μm .

Where the film of the invention coated with the described coating materials is used for vehicle bodies and for that purpose is to be additionally coated with

a surfacer composition, it is possible with preference to use surfacer compositions suitable for coating automobile bodies. Here again, the flexibility must be sufficient for the purposes of the invention. In accordance with the invention, this flexibility can be controlled by way of the degree of crosslinking.

The surfacer coat obtained in this way has essentially three functions: firstly, it is intended to compensate for the unevennesses and secondly to improve the resistance of the overall coating system to stone chipping. Moreover, the surfacer serves to promote adhesion between film polymer and coating system. For this purpose, the surfacer may comprise the adhesion promoting agents mentioned in connection with the liquid coating material. The surfacer compositions may consist essentially of a binder, a crosslinking agent, pigments and fillers, and, if desired, further additives, such as crosslinking catalysts and leveling auxiliaries, for example.

As binders, the surfacer compositions which can be used may comprise epoxy resins, polyester resins, polyurethane resins, polyacrylate resins and alkyd resins, or combinations of such resins. As crosslinking agents, the surfacer compositions which may be used may comprise amino resins, such as for example, melamine-formaldehyde resins, amines, polyisocyanates and carboxyl-containing compounds. Examples of pigments which may be present in the surfacer compositions which may be used are titanium dioxide, phthalocyanines, iron

oxides and carbon black. As fillers, the surfacer compositions may for example comprise lime or barium sulfate.

Suitable materials for the support layer that is to be coated include all thermoplastics such as polyolefins, polyesters, polyamide, polyurethane, polyacrylate, especially copolymers of acrylonitrile, styrene, acrylic esters (e.g., grades of LURAN and LURAN S.). Also suitable of course are blends of different thermoplastics, for example, of polycarbonate and polybutylene terephthalate. Likewise suitable are mixtures of the aforementioned substances. The film thickness may be between 10 and 1 000 μm , preferably from 10 to 500 μm , most preferably from 20 to 250 μm , and is guided only by practical aspects for the processing.

In addition to the abovementioned materials, self-supporting paint films may also be used as the support layer. Such paint films are described, for example, in DE 195 35 934.

A transparent polymer film may be applied to the layer based on the above-described powder coating materials or powder coating dispersions. For this film it is possible in principle to use the materials which are also suitable for the support film. For reasons of cost, polyolefin films are preferred.

The films coated in accordance with the invention may be rolled up. Consequently, the products may be offered and supplied in the form of rolls. For

this reason, the coating materials used in accordance with the invention must have a flexibility which is sufficient for rolling up.

In accordance with the invention it may be
5 envisaged not to obtain a continuous film layer of the powder coating material or of the powder clearcoat dispersion in the unprocessed state of the film, but instead to apply a very close packing of material particles having average diameters of less than 50 μm ,
10 preferably less than 15 μm , with particular preference less than 10 μm , to the film or to a film provided with a pigmented layer based on a liquid coating material. The particles of material have preferably a melting point of from 50 to 150°C, preferably from 70 to 100°C
15 and are sintered with one another (locally bonded at the points of contact) to such an extent that the coated film can be wound up without problems.

Accordingly, the powder coating dispersion or the powder coating material is preferably present in
20 sintered, partially crosslinked form or - in the case of the powder coating dispersion - in dried form.

In processing, the film may be formed even at temperatures below the melting point of the particles. In this case, the particles bonded locally to one
25 another may be separated at their contact points. In the case of local severe deformation, it is possible in this case for macroscopic, visually perceptible cracks to appear in the layer. Since in this state the material is still completely uncrosslinked, the cracks

may subsequently be closed by passing thermal energy through the flowing material (when the film is used to decorate thermoplastic parts, this takes place preferably in the injection mold as a result of the hot polymer mass). In this state, the final curing of the material may also then take place. Said final curing may take place optionally by a thermally (catalyzed or not) proceeding chemical crosslinking (preferably addition reactions without notable emissions of, for example, masking agents). The thermal crosslinking may preferably take place while still in the injection mold, and/or by the action of hot media (e.g., circulating air) on the molding already provided with the film. The result obtained comprises fully cured films having excellent appearance (surface smoothness, gloss) and very good service properties (corresponding to known OEM clearcoat technologies).

The films may in principle also be applied to all molding blanks, preferably metal panels, which are suitable for producing vehicle bodies, surface-mounted parts for vehicle bodies, domestic appliances, e.g., refrigerators, washing machines, dishwashers. Predominantly, the films are applied to pretreated metal panels. These panels may have been pretreated by phosphating and/or chromating, for example.

The coated films prepared as described above may be laminated on to the surface of a molding blank, i.e., of an as yet unformed substrate, preferably a metal panel. In this case, the film may first be

laminated on to the unformed substrate, followed by forming of the substrate, and finally by the formation of a film, and curing thereof.

Adhesion to the surface to be coated may be brought about in a variety of ways. One possibility, for example, is to use films which have adhesion promoting groups, such as urethane groups, acid anhydride groups or carboxyl groups, for example, or films which have been provided with adhesion promoting groups by coextrusion with a polymer containing adhesion promoting groups. The adhesion between the film and the surface that is to be coated may also be brought about by the use of an adhesive. In this case, use may be made both of adhesives which are solid at room temperature and of adhesives which are liquid at room temperature.

Implementation examples

1. Preparation of the acrylate resin

21.1 parts of xylene are introduced as an initial charge and this charge is heated to 130°C. The following are metered into the initial charge at 130°C over the course of 4 h by way of two separate feed vessels: initiator: 4.5 parts of TBPEH (tert-butyl perethylhexanoate) mixed with 4.86 parts of xylene, and monomers: 10.78 parts of methyl methacrylate, 25.5 parts of n-butyl

methacrylate, 17.39 parts of styene and 23.95 parts of glycidyl methacrylate. The mixture is subsequently heated to 180°C and the solvent is stripped off under reduced pressure < 100 mbar.

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1.1. Preparation of the powder clearcoat material

77.5 parts of acrylate resin, 18.8 parts of dodecanedicarboxylic acid (acid curing agent), 2 parts of Tinuvin 1130 (UV absorber), 0.9 parts of Tinuvin 144 (HALS), 0.4 parts of Additol XL 490 (leveling agent) and 0.4 parts of benzoin (devolatilizer) are intimately mixed on a Henschel fluid mixer, the mixture is extruded on a BUSS PLK 46 extruder, the extrudate is ground on a Hosokawa ACM 2 mill, and the milled material is sieved off through a 125 µm sieve.

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1.2. Preparation of the dispersion

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0.6 parts of Troykyd D777 (defoamer), 0.6 parts of Orotan 731 K (dispersing auxiliary), 0.06 parts of Surfinol TMN 6 (wetting agent) and 16.5 parts of RM8 (Rohm & Haas, nonionic associative thickener based on polyurethane) are dispersed in 400 parts of deionized water. Then 94 parts of the powder clearcoat material are introduced in small portions, with stirring. Subsequently, a further 0.6 parts of Troykyd D777, 0.6 parts of Orotan 731

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K, 0.06 parts of Surfinol TMN 6 and 16.5 parts of RM8 are incorporated by dispersion. Finally, 94 parts of the powder clearcoat material are introduced in small portions, with stirring. The material is milled in a sand mill for 3.5 h. The finally measured average particle size is 4 μm . The material is filtered through a 50 μm filter and, finally, 0.05% Byk 345 (leveling agent) is added.

1.3. Application of the dispersion

The slurry is applied by means of a gravity flow cup gun to steel panels coated with aqueous basecoat material. The metal sheet is flashed off at room temperature for 5 minutes and at 60°C for 5 minutes. Subsequently, the metal sheet is baked at a temperature of 140°C for 30 minutes.

At a film thickness of 40 μm , a high-gloss clearcoat film with MEK resistance (> 100 double strokes) is produced.

The condensation resistance of the clearcoat film is good.

2. Production of a film coated with clearcoat composition.

2.1 Film coated with polymer

5 A 400 μm thick film of acrylonitrile-styrene-acrylate copolymer (LURAN S 797, BASF AG) is rollercoated with a commercially customary aqueous basecoat material for automotive coatings and is dried by passing it through a segmented convection oven with heated air with a temperature gradient from 40 to 100°C and a residence time of two minutes so as to give a tack-free film without thermosetting crosslinking. The dry film thickness is 50 μm . The suspension obtained in 1.2 is applied by roller blade application to the basecoat thus obtained. The evaporation of the water and the pointwise binding of the dried polymer particles takes place during two-minute passage through a segmented convection oven whose air has a temperature gradient between 50 and 100°C. The result is a blocking-free, non-flowing film with a 70 μm thick, nontransparent, white clearcoat, which is windable and storable.

2.2 Forming and curing of the film

25 The film is bent around a cylinder by its uncoated side at room temperature. The formed film remains crack-free (cylinder diameter ≥ 10 cm) or exhibits increasingly macroscopic cracks in the white clearcoat (cylinder diameter < 10 cm). After

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change in the film, and no loss of adhesion following one-hour regeneration of the films in the ambient air.